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EVIDENCE AGAINST HYDROGEN CRACKING IN GUN BORES: A REPLY

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13. ABSTRACT *(Maximum 200 words)*

The present report is a reply to J.H. Underwood's critique of the ARDEC Technical Report entitled "Gray Layers and the Erosion of Chromium Plated Gun Bore Surfaces" by Cote and Rickard. At issue is the evidence from the survey study by Cote and Rickard, that hydrogen cracking plays no role in damage initiation and chromium spallation.

A brief review of the controversy relating to hydrogen cracking and damage initiation in gun bores is presented here. The question of hydrogen cracking beyond the initiation stage is also addressed. Consideration of some of the implications of the proposed hydrogen-cracking model and the general observations of the survey study offer reasons to doubt that damage initiation in gun bores is a result of hydrogen cracking, despite the plausibility of the proposed model.

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TABLE OF CONTENTS

LIST OF ILLUSTRATIONS

INTRODUCTION

Cote and Rickard (ref 1) reported on a survey study of damage initiation and chromium spallation in five different gun tubes. One of their findings was that hydrogen cracking did not appear to be a factor, at least in the initial stages of damage of the steel substrate under the protective chromium plate. Underwood (ref 2) disagrees with that observation and maintains that hydrogen cracking is the root cause of all erosion processes in the first 500 microns into gun bore surfaces, including chromium spallation. The idea that hydrogen cracking may be a factor is plausible, given the presence of hydrogen in the propellant gases. Since there are plausible, alternative mechanisms and basic erosion mechanisms are yet to be established, a critical assessment of the proposed new mechanism is in order. The basic problem with confirming or disproving the hydrogen cracking explanation is the high mobility and elusive nature of hydrogen, and, in this case, the absence of clear hydrogen cracks, especially in the initiation stages of damage. An attempt to address these issues is presented here.

REVIEW OF COTE AND RICKARD FINDINGS

Cote and Rickard (ref 1) reported on a survey study of damage initiation to the steel beneath the chromium plating in fired gun bores of three 120-mm and two 155-mm tubes. The central consideration was the relationship between damage initiation and chromium spallation. It was found that gas-metal reaction products were preserved in the relatively protected regions in the steel at the tips of fine chromium cracks. These reaction products are most clearly delineated in unetched specimens where they are manifested as distinct gray zones or layers. These gray layers tend to propagate beneath the chromium to undermine the coating. Electron microprobe analyses showed them to be comprised of iron oxides, iron sulfides, or mixtures of the two. Wherever a heat-affected zone occurs, the familiar "white layer" is always seen outlining the gray layers, so that carburization (and nitriding) also occurs simultaneously with the high-temperature oxygen and sulfur attack. As described in the National Defense Research Committee Report (ref 3), these types of reaction products have long been known to occur on unplated gun bore surfaces. The new feature reported in Reference 1 is the universal presence of sulfur, oxygen, and carbon attack at the tips of fine chromium cracks.

Because of the relatively isotropic nature of the corrosion at the chromium crack tips, and the relatively high volume of steel consumed at that site, it is concluded that fracture in uncorroded steel is not central to damage initiation beneath the chromium. The micrographs in Reference 1 offer straightforward illustrations of the dominant role of chemical attack. Figure 1 is reproduced from that report as an example. The image is from specimen 2, which is a tube that had experienced 220 conventional rounds and 80 experimental high-temperature rounds. The undermining of the chromium coating is clearly shown. Evidence of sulfur, oxygen, and carbon attack (white layer) are all present in this figure. The entire length of the extended erosion pit is coated with a gray layer (iron sulfide).

Regarding the propagation of damage into the steel beyond initiation, it is evident that fissures through the brittle reaction products provide direction for propagation of chemical attack. It is also significant that the high-temperature corrosion damage tends to terminate with rounded blunt features. Propagation through corroded grain boundaries is also likely in view of the evidence for substantial diffusion required to form thick reaction zones despite short exposure times per round. (Earlier simulation studies at moderate flame temperatures showed an iron sulfide layer forming at a rate of 0.5 micron in thickness per round [ref 3]). As damage propagates into the bore beyond the corrosion zones, or in tube locations where high-temperature attack is not a factor, it is expected that the usual mechanical fatigue and fracture processes will prevail, and true (corrosion-free) metal fracture can occur.

(A note on terminology used in Reference 1 and in the present report: In an attempt to improve clarity in discussions of the many processes, we reserve the terms *fracture* and *crack* for cracks in uncorroded steel; that includes hydrogen cracks, since the hydrogen is mobile and thought to act primarily at surfaces. The term *fissures* is applied to cracks through brittle-reaction products. Where there is evidence for corrosion, melting, and other high-temperature contributions, we use the terms *crack-like damage.*)

Another finding in Reference1 is that chromium spallation generally initiates by failure in the chromium or along the chromium/steel interface. No instances of spallation by fracture of the underlying steel were observed in the survey. A related observation is evidence for sliding wear as a key factor in the mechanical damage of the chromium especially in the 155-mm cases.

Finally, the specific issue here is our conclusion (ref 1) that the hydrogen-cracking mechanism proposed by Underwood and Parker (ref 4) is inconsistent with the observed progression of high-temperature corrosion into the steel at the chromium crack tips. Hydrogen cracking is expected to occur at or near room temperature and at atmospheric pressure. Thus, such cracks should be manifested as corrosion-free and debris-free narrow cracks. The proposed hydrogen-cracking mechanism involves interaction of the tensile stress layer (estimated at 500 microns deep), formed on cooling in the heat-affected layer of steel, with the hydrogen supplied by earlier exposure to the high-temperature propellant gas. The distinguishing feature of this proposed mechanism is that the hydrogen cracks ought to be substantially developed (several hundred microns deep) after the first few rounds since the stress layer and the hydrogen are both present after the first few rounds. Such rapid, early fracture is inconsistent with the general observations (ref 1) of relatively slow, gradual progression of corrosion damage into the steel (e.g., Figure 1).

UNDERWOOD'S CRITIQUE OF REFERENCE 1

Underwood (ref 2) disagrees with the conclusion in Reference 1 relating to hydrogen cracking and states, "...hydrogen cracking is the initial cause of chromium loss, and gray layer formation [gas-metal reaction products] is a consequence of hydrogen cracking." His evidence is the shape of the cracks in the first few hundred microns of steel that look like hydrogen cracks because of their meandering nature. His view is that all cracks that form in the first 500 microns in gun bores are hydrogen cracks (formed at room temperature after hydrogen charging at high temperatures by the hydrogen-rich propellant) because the calculated (ref 4) tensile stress zone extends to that depth. In the proposed mechanism, other factors such as fatigue and fracture from firing stresses, corrosion effects, and sliding wear play no role in damage initiation and propagation in the first 500 microns. Spallation is said to occur as a result of the joining up of hydrogen cracks in the steel; this type of spallation results in the loss of a section of chromium plated steel. Underwood (ref 2) also maintains that propagation of the high-temperature corrosion damage into steel must be aided by hydrogen cracking.

RESPONSE TO CRITIQUE

The main question in Reference 1 regarding the absence of a rapid development of deep hydrogen cracks required by the Parker and Underwood mechanism (ref 4) is not addressed in Underwood's critique. In our view, the damage propagation in the examples given in Reference 1 is too slow (requiring from hundreds to thousands of rounds in a highly corrosive, high-temperature environment in these examples) to support invocation of enhanced fracture by the proposed hydrogen-cracking mechanism.

To retain the hydrogen-cracking model in the absence of early, rapid cracking, a slow mode scenario is suggested (see references in Reference 2) where the hydrogen is effectively metered out in small doses with each round so that the hydrogen cracking progresses in relatively small increments after every round. This, too, is inconsistent with the data because the required hydrogen-crack increment that should have formed on cool-down after the *last* round is never observed. The absence of such cracks cannot be explained by metal consumption through corrosion because these cracks are to be produced *after* each round at room temperature and atmospheric pressure. Such cracks should easily be distinguishable from high-pressure/temperature damage through fineness of the crack and the absence of corrosion and firing debris within the crack.

The view (ref 2) that rapid fracture *must* play a role in propagation of damage into the steel is addressed next. It was suggested in Reference 1 that fracture through corroded grain boundaries or through mechanical fatigue and fracture (where there is no corrosion) can also contribute to damage propagation. Hydrogen cracking is considered unlikely, however, for the reasons cited above. It is not clear that fracture into uncorroded steel *must* play a role in the early stages of damage propagation, especially where corrosion rates are high. Consider the results in Figure 1, which has the deep corrosion pits with only 300 total rounds. Assuming the empirically-determined 0.4 micron per round rate of iron sulfide layer formation in propellant environments, and assuming a film rupture process with fresh metal exposure through the sulfide fissures with each firing, one estimates corrosion pit depths of 120 microns. (The estimate is conservative because it ignores the observed diffusion enrichment of the steel by sulfur beneath the scale (~0.3 micron per round)). The estimate is in accordance with the corrosion pit depth of 100 microns in Figure 1, so that rapid fracture of steel is not essential to explain the shape of extended corrosion pits.

The above discussion regarding chemical effects and damage initiation is supported by work on the origin of bore cracking reported in the National Defense Research Committee report (ref 3). It was shown that small alterations in the propellant chemistry can dramatically affect and even eliminate bore surface cracking. The report concludes that chemical effects determine initial fracture (heat-check) behavior of gun bore surfaces.

Another point is that no direct experimental evidence exists, to date, to show that the steel areas in the first 500 microns of gun bores possess an enhanced hydrogen concentration after firing. This would seem to be an essential step in establishing the viability of the proposed hydrogen-cracking model. The results in the present paper indicate an oxidizing atmosphere in cracks because of the rapid formation of oxide and sulfide layers. It is known that even ppm levels of oxygen and sulfur gases can significantly inhibit embrittlement in steels by high-pressure hydrogen (ref 5). Thus, a high hydrogen concentration in firing environments may not be a sufficient condition for hydrogen embrittlement.

Finally, there is a danger that focus on hydrogen cracking alone as the root cause of erosion can lead to ineffective approaches in resolving the erosion problem. It is often recommended that a nickel underlayer (ref 4) be used for chromium for erosion resistance because nickel is a barrier coating for hydrogen. It cannot be overlooked that nickel coatings in various forms, including underlayers, were tried in the 1940s (ref 3) and failed to provide any enhanced resistance to erosion. This failure was attributed to the high reactivity of nickel with propellant gases such as hydrogen sulfide. Grain boundary attack of nickel was often observed. (Cobalt underlayers were found to be beneficial because of their resistance to chemical attack by propellant gases.) Thus, the available body of pertinent firing data indicates that nickel will not work on gun bores.

On the other hand, nickel has been successfully applied on a breech-end closure to prevent severe early cracking (ref 6). This cracking is intergranular and the interpretation in terms of hydrogen cracking seems persuasive. One possible reason for the apparent discrepancy with earlier negative results on bore surfaces is the fact that the breech closure is beneath a combustible case and experiences far lower temperatures than the bore surface.

NEW DATA

Some new data are presented to help clarify the points on this issue and to expand the discussion beyond damage initiation.

Given the reliance on a meandering crack shape and branching to establish hydrogen cracking, it is useful to examine the shape of fatigue cracks that are produced by pure mechanical loading in a simulated fatigue test using hydraulic pressure. Figure 2 shows results on a 120-mm specimen that had developed significant erosion pits by firing 1246 conventional rounds prior to mechanical testing, where 6593 cycles were applied at 97,600 psi. Hydraulic pressure cycling was applied to develop fatigue cracks for the purpose of establishing safe service lives of eroded tubes. In these specimens, such cracks are easily distinguished from those due to firing because of their narrow widths, long lengths, and absence of corrosion products and firing debris. It can be seen that the fatigue crack grown under purely mechanical cycling has all the features attributed to classic hydrogen cracks. The longest crack in this specimen was approximately 1-cm in length and exhibits all the features associated with environmental cracking, including branching all the way to the crack tip. This is twenty times deeper than the estimated tensile stress zone (ref 3), so it cannot be attributed to the proposed hydrogen-cracking mechanism. The mean crack growth rate for this mechanically driven crack is over one micron per cycle. Thus, rapid cracking and crack shape are insufficient to establish hydrogen-cracking mechanisms in gun tubes. The usual mechanical fatigue cracks may easily be mistaken for hydrogen cracks with those criteria.

Figure 2 also shows a spalled section of chromium that is typical of what is observed in the survey study (ref 1). In general, the spallation is at or near the chromium/steel interface and as can be seen in this figure, there is no joining of cracks in the steel beneath the chromium.

Figure 3 is a scanning electron micrograph (SEM) of typical reaction products that form at the tips of the cracks in the chromium coating for the same specimen as in Figure 1. The fractures in the SEM images are better defined than in optical micrographs. This is the typical result, which provides a straightforward illustration that fracture into uncorroded steel is not observed in early stages of damage. Thus, as illustrated by this figure and by the data in Reference 1, there is no evidence for the predicted incremental hydrogen cracks that are supposed to form at room temperature and pressure (according to the slow mode scenario) after the last round. The only observed fractures are in the form of fissures in the brittle reaction products (sulfides and oxides); these serve to direct the progress of the gas-metal attack into the steel.

All earlier discussions focused on damage initiation. Figure 4 shows the opposite extreme, that is, several of the deepest fractures in specimen 2. These fractures occurred in a section where the chromium coating and several millimeters of steel had been eroded away. Cracks resembling the one at the left in the figure are used to show that hydrogen cracking may be present since it is assumed (ref 2) that mechanical fatigue alone cannot produce cracks of this length (in 300 rounds). As illustrated in Figure 2, however, this deep, branching, crack pattern is, in fact, consistent with mechanical cracking.

The majority of the deep cracks in this sample resemble the crack at the right in Figure 4 with its blunt crack tip. Crack blunting in deep cracks is probably not due to ductile fracture, since the irregular surface morphologies at the tips do not give the appearance of plastic flow. Regarding the hydrogen cracks that are supposed to form after each firing, one never observes the sharp debris-free hydrogen cracks emanating from any of the numerous blunt cracks in these specimens.

Another notable feature is the general widths of the cracks. Comparison of cracks in Figure 4 with the room-temperature cracks from mechanical loading in Figure 2 show crack widths are, in most cases, roughly a factor of five larger when produced under firing conditions. This suggests a high rate of material removal via gas-metal attack, even for deep cracks in fired tubes. While there are no observable reaction products (gray layers) in the steel at the tips of these deep cracks, there is evidence of firing debris all along the cracks. For example, energy dispersive x-ray analysis shows aluminum deposited (from the projectiles) and potassium along the full length of even the deepest cracks, indicating exposure to hot gas attack at the crack tips.

SUMMARY

The available evidence indicates little need for the high-rate cracking associated with hydrogen effects to explain the gas-metal corrosion observations in damage initiation into the steel substrate in gun bores. The corrosion that runs immediately underneath the chromium plate clearly cannot require fracture of the steel. Any cracking that is observed relative to damage initiation is generally confined to fissures within the reaction products. Another point is that crack joining in the steel beneath the chromium is not observed to be the general cause of chromium plate spallation. The evidence (ref 1) indicates, that other factors, such as the sliding mode of chromium fatigue cracking (from projectile passage), are responsible for spallation on gun bore surfaces. Spallation rates will be enhanced by any gas-metal reactions (gray layers) that form beneath the chromium plate.

The discussion in Reference 1 focused on initiation of damage and chromium spallation, but the data (absence of any precursor cracks) from the five different gun tubes also provide indications that the proposed hydrogen-cracking mechanism is not occurring in gun bore surfaces. On the other hand, given the plausibility of the mechanism, it must be acknowledged that hydrogen cracking remains a valid concern.

REFERENCES

1. Cote, P.J., and Rickard, C., "Gray Layers and the Erosion of Chromium Plated Gun Bore Surfaces," Technical Report ARCCB-TR-99016, Benet Laboratories, Watervliet, NY, September 1999.

2. Underwood, J.H., "Critical Comments on Report Titled '*Gray Layers and the Erosion of Chromium Plated Gun Bore Surfaces*' by Cote and Rickard," Technical Report ARCCB-MR-00006, Benet Laboratories, Watervliet, NY, April 2000.

3. Burlew, J.S., ed., "Hypervelocity Guns and the Control of Gun Erosion," Summary Technical Report of the National Defense Research Committee, Division 1, Office of Scientific Research and Development, Washington, DC, 1946.

4. Underwood, J.H., Parker, A.P., Cote, P.J., and Sopok, S., *Transactions of the ASME*, Vol. 121, February 1999, pp. 116-120.

5. Chandler, W.T., and Walter, R.J., "Hydrogen Embrittlement Testing," ASTM STP 543, American Society for Testing and Materials, 1974, pp. 170-197.

6. Troiano, E., Vigilante, G.N., Underwood, J.H., and Mossey, C., "Analysis of a Piston Experiencing Environmentally-Assisted Cracking as a Result of Compressive Overloading," Technical Report ARCCB-TR-99010, Benet Laboratories, Watervliet, NY, June 1999.

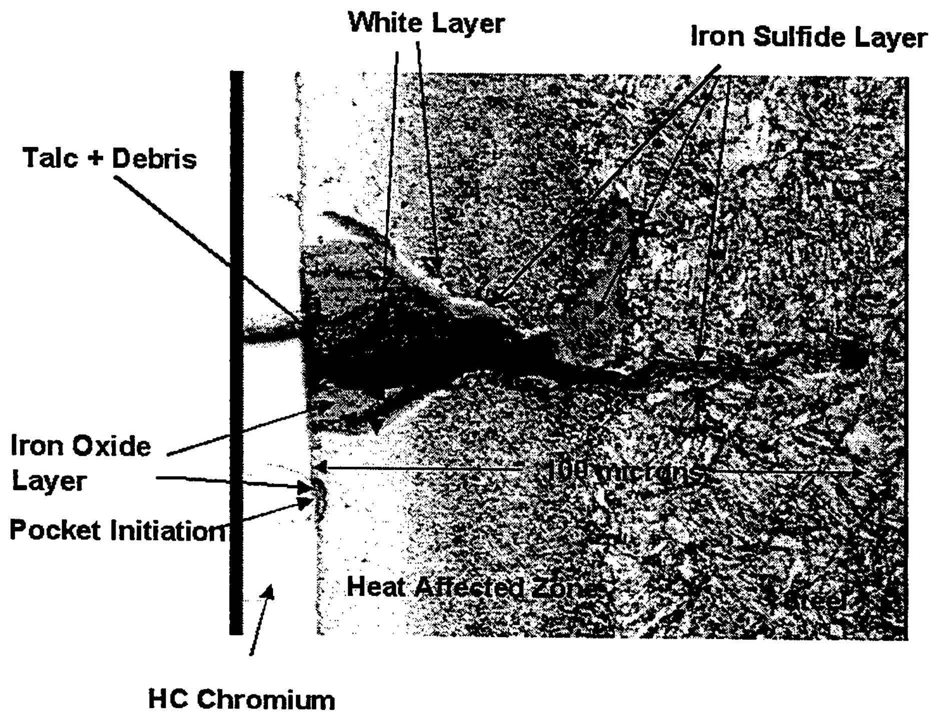

Figure 1. Initiation and propagation of high-temperature corrosion into the gun bore surface beneath the chromium coating.

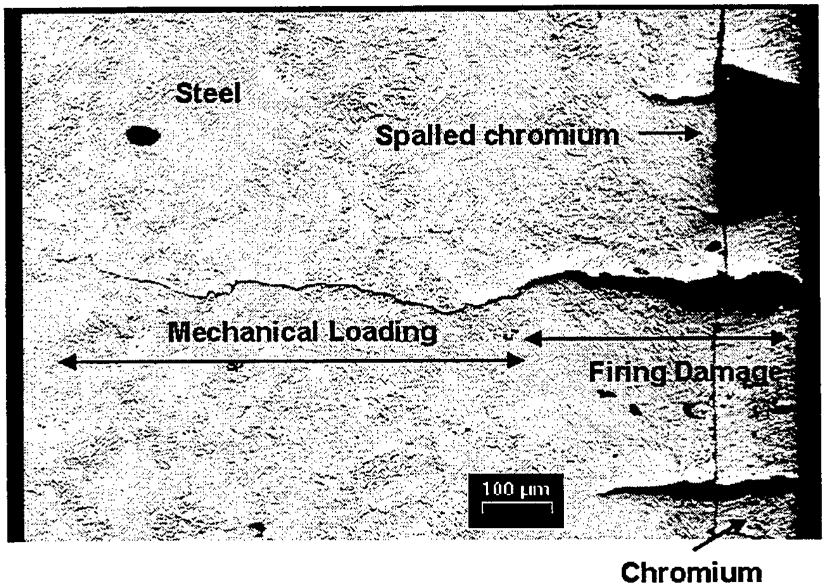

Figure 2. Portion of the fatigue crack generated by mechanical loading seen to have the same meandering, branching nature usually attributed to classic hydrogen cracking.

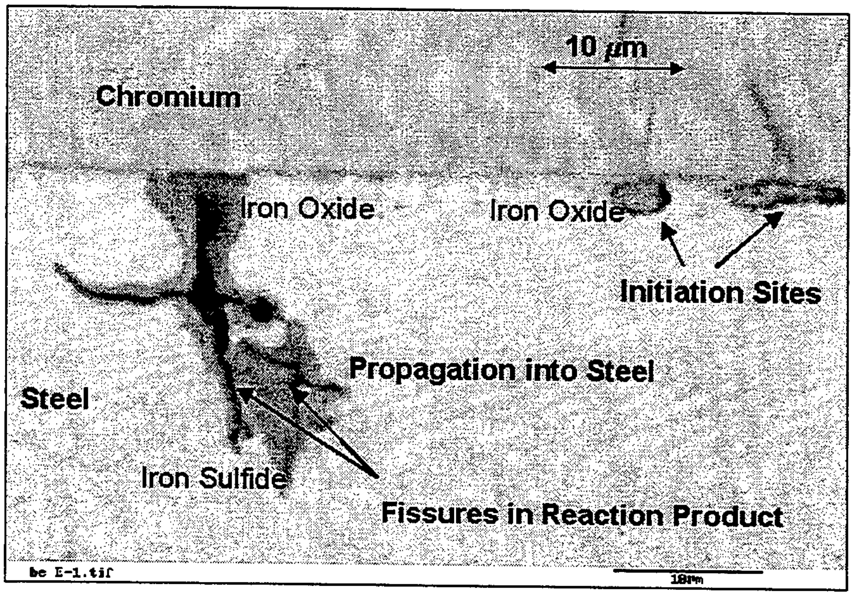

Figure 3. SEM illustrating that fracture into uncorroded steel does not occur during initiation of damage beneath the chromium coating.

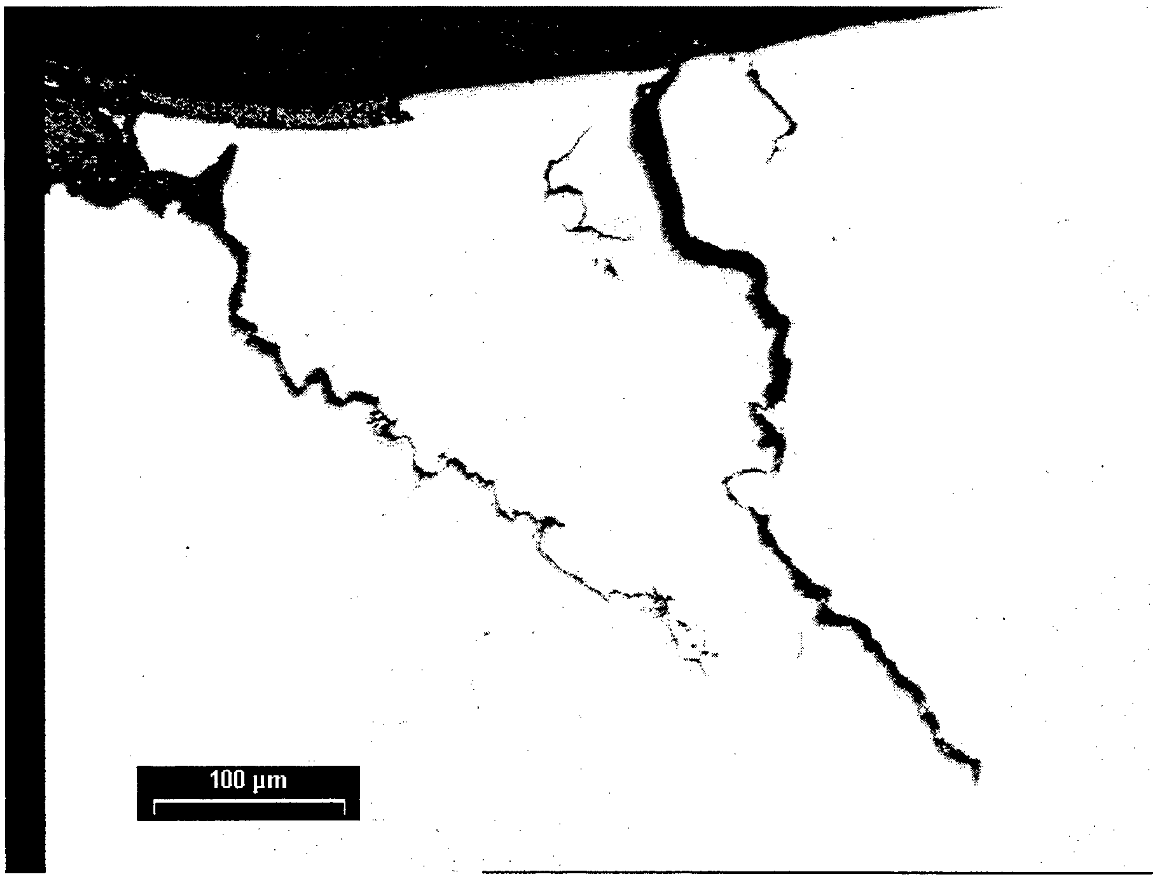

Figure 4. Micrograph showing examples of the most severe fractures in specimen 2.

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